THERMAL-METALLURGY OF ZINC ALLOYS

BY

AMBROSE ALLEN ARNOLD

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1921

UNIVERSITY OF ILLINOIS

May 31, 1921

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

AMBROSE ALLEN ARNOLD

ENTITLED THERMAL-METALLURGY OF ZINC ALLOYS

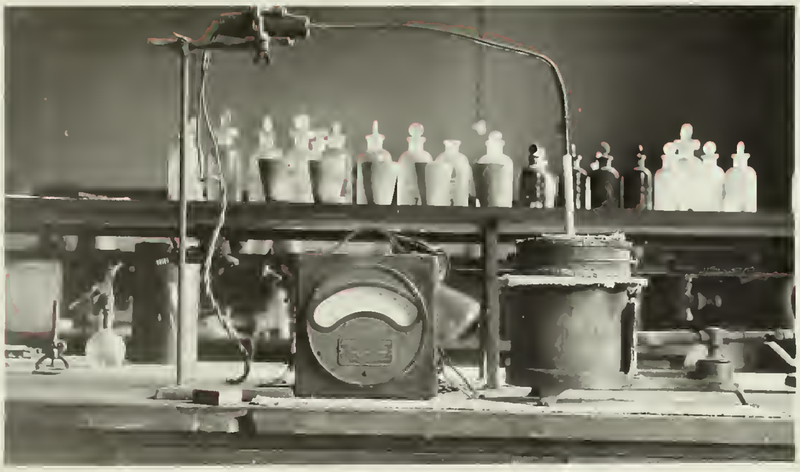
IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering

B S Hopkins
Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF CHEMISTRY



C-O-N-T-E-N-T-S

THERMAL METALLURGY OF ZINC ALLOYS

Zinc is practically in its infancy as far as its possible exploitation of uses is concerned. In order to discover new applications it is necessary to understand zinc and its varying conditions. That has been the object of this investigation -- How does Zinc behave when alloyed with certain other metals?

In order the better to understand metals, a comparatively new branch of scientific endeavor has recently been given more attention -- that of Physical Metallurgy. The scope of Physical Metallurgy is exceedingly wide and makes generous use of chemistry, physics, mechanics (strength of materials), crystallography, and Thermal analysis.

It is in part to the latter division -- thermal analysis -- that this study directs itself in so far as certain Zinc alloys are concerned -- Zn--Sn, and Zn - Pb - Sn - although thermal relations of metallic alloys have been given some attention, it is a comparatively new consideration and much work remains to be done. A survey of the literature gave no evidence of any work along the lines of this particular investigation, alloys of zinc and tin, and of zinc lead, and tin. Excellent work had been carried on with some of the more common alloys used in everyday metallurgical practice, notably that of iron, carbon, and copper, and also a few zinc combinations. A study of the changes which occur when metals are heated and cooled has thrown much light on the constitution of those metals and their alloys. The following have done work along these lines:-

Metallic Alloys	William T. Brannt.
Introduction to Physical Metallurgy	Walter Rosenhain
Metallurgy of the Common Metals	

The Physical Chemistry of the Metals Rudolph Schenck.
Translated by Reginald Scott Dean.

Traite de Metallographic Felix Robin

The Elements of Metallography Rudolph Ruer.
Translated by C. H. Mathewson.

Chemische Technologic Der Legierungen Dr. P. Runglass

A Treatise on Brasses, Bronzes, and other Alloys Robert H. Thurston.

Metallogrphy Cecil H. Desch.

Alloys and their Industrial Applications, Edward F. Law.

There are various methods of making cooling curves, depending upon methods of heating and methods of plotting. For heating purposes, furnaces of the gas or electical resistance types are commonly employed. In this investigation a gas furnace was used. There are three distinct methods of plotting data: first, "time - temperature," which is simplest and gives behavoir of metal in most direct way; second, "inverse rate," for which the observer notes the time intervals occupied by the metallic solution in rising or falling through successive equal differences of temperature and plots a curve whose ordinates are T (temperature) and whose abscissae are $\frac{dt}{dT}$ where t is time and T is temperature; third, the "differential" and "derived differential" in which the rate of heating or cooling of the metal under investigation is compared with a standard piece of metal placed in the same furnace and treated under the same conditions at the same time. In this investigation the first, or "time-temperature" method of plotting cooling curves was followed. It is easily the simplest and for this purpose seemed sufficiently adequate.

The procedure was simply to get a melt of the alloy, insert a thermo couple and read temperature as it cooled, at one minute intervals, and plot the data on graph paper. Wherever a flattening of the curve is evident, at that temperature a solidification took place.

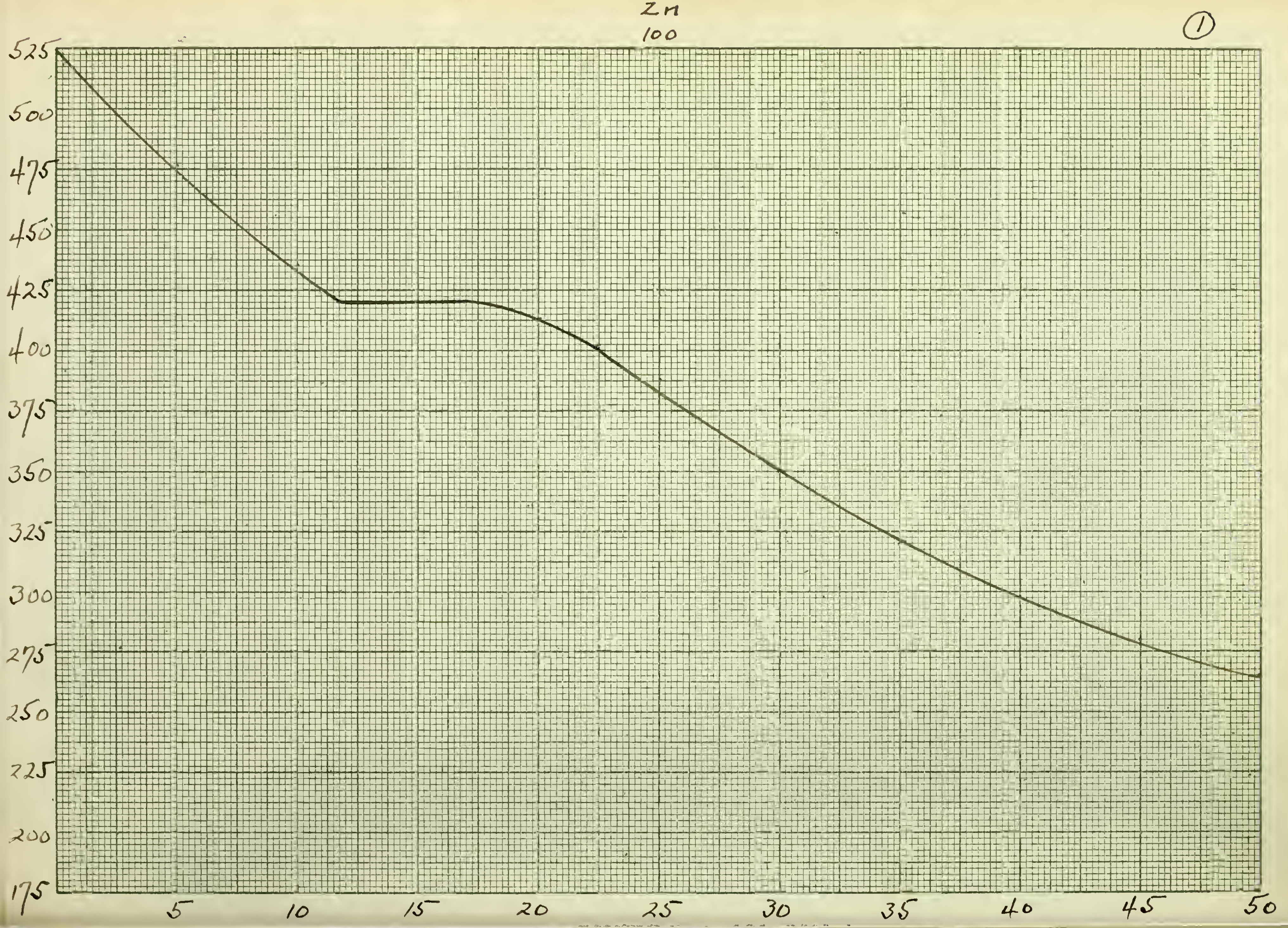
An ordinary pot furnace was used into which air and gas in proper proportions, admitted under the usual laboratory pressures, were burned. This furnace was thoroughly saturated with heat to a temperature several hundred degrees higher than that required for the melt in order that the radiation of heat might be slower and more uniform. This is an important precaution as was learned by experience. A mixture of the metallic constituents in granulated form, chemically pure, 200 grams in weight, was placed in a fire clay crucible and covered with about one quarter inch of pulverized bone charcoal. The crucible and its contents were then placed in the furnace until a good melt was assured. The heavy covering of bone charcoal prevented oxidation. The melted solution was then thoroughly stirred with a steel spatula, a thermo couple inserted into the melt, the gas and air turned off, all openings carefully covered with heavy asbestos sheets, and the regular readings were then taken. The graphs show that all readings were begun at 525 C. As a matter of fact the cooling usually started at 600 C. By the time the thermo couple indicated 525 C the rate of heat radiation was quite uniform. While the diagrams indicate only fifty minutes for each "run", some of the melts were continued for longer periods with the same evidence -- namely, that the cooling continued to drop regularly.

A portable Hoskins, type (PA), pyrometer, frequently

calibrated, was constantly used throughout.

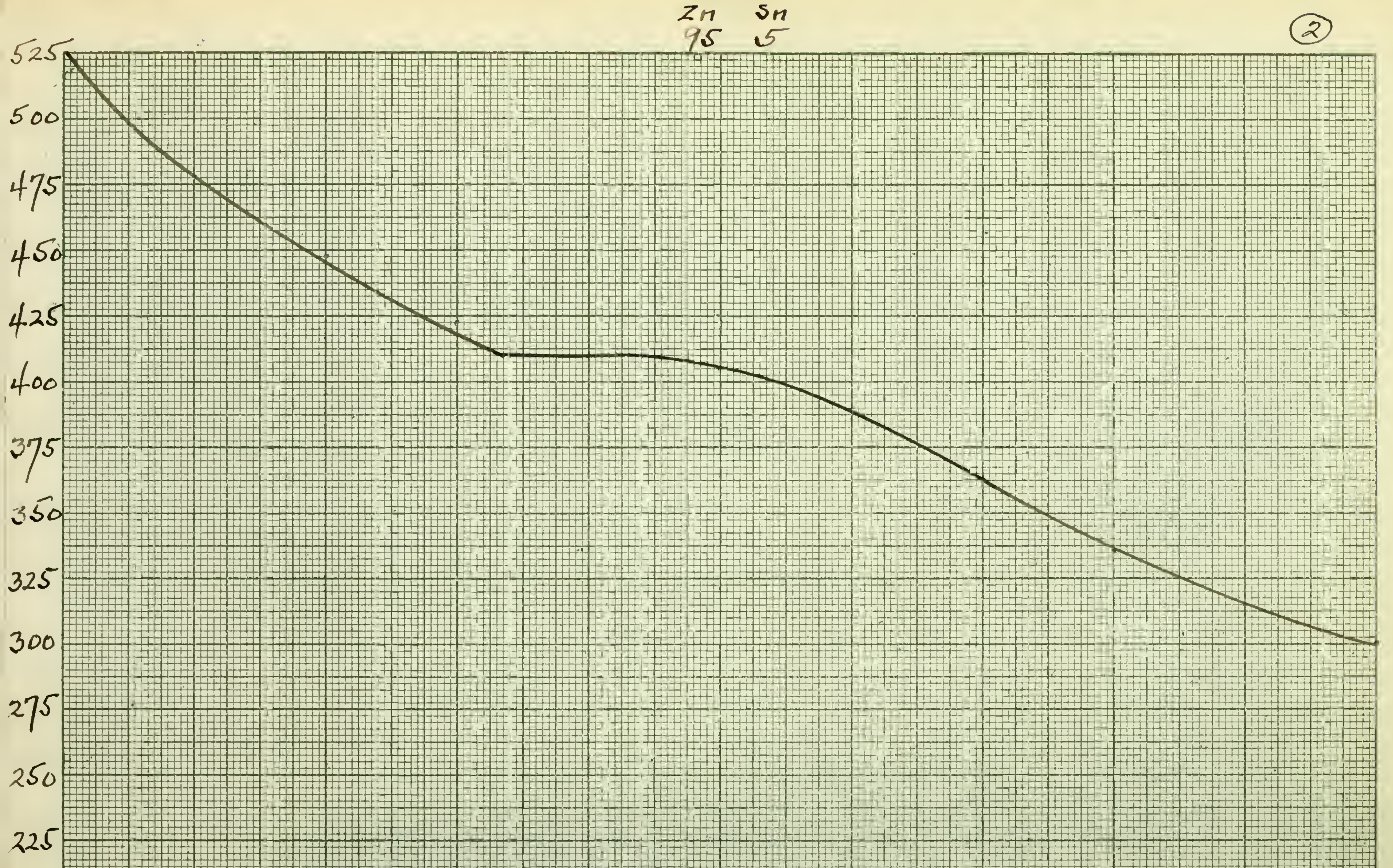
The melting points of the metals concerned are as follows:-

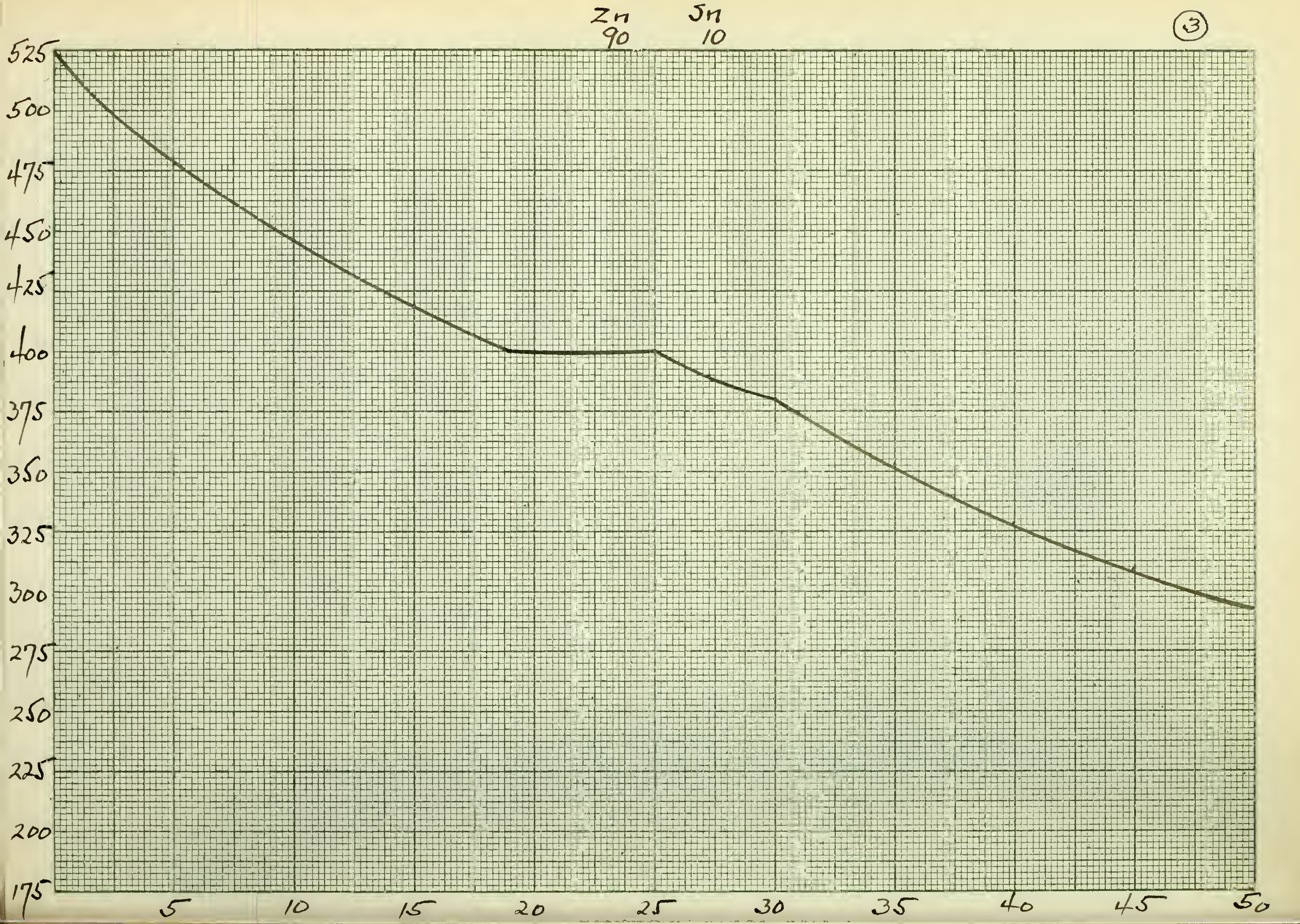
Zinc	419 C
Lead	327 C
Tin	232 C



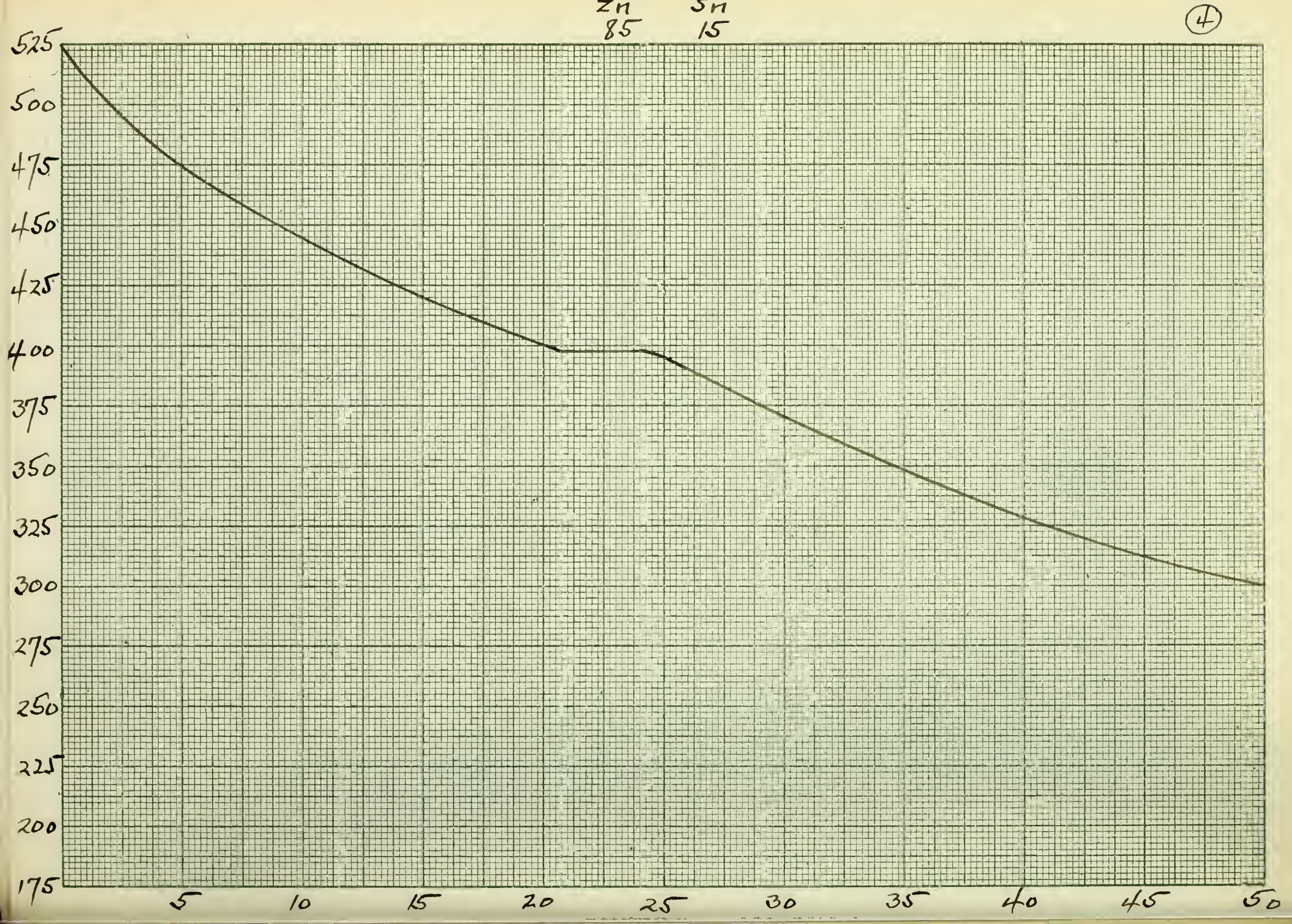
Zn
100
1
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

(2)

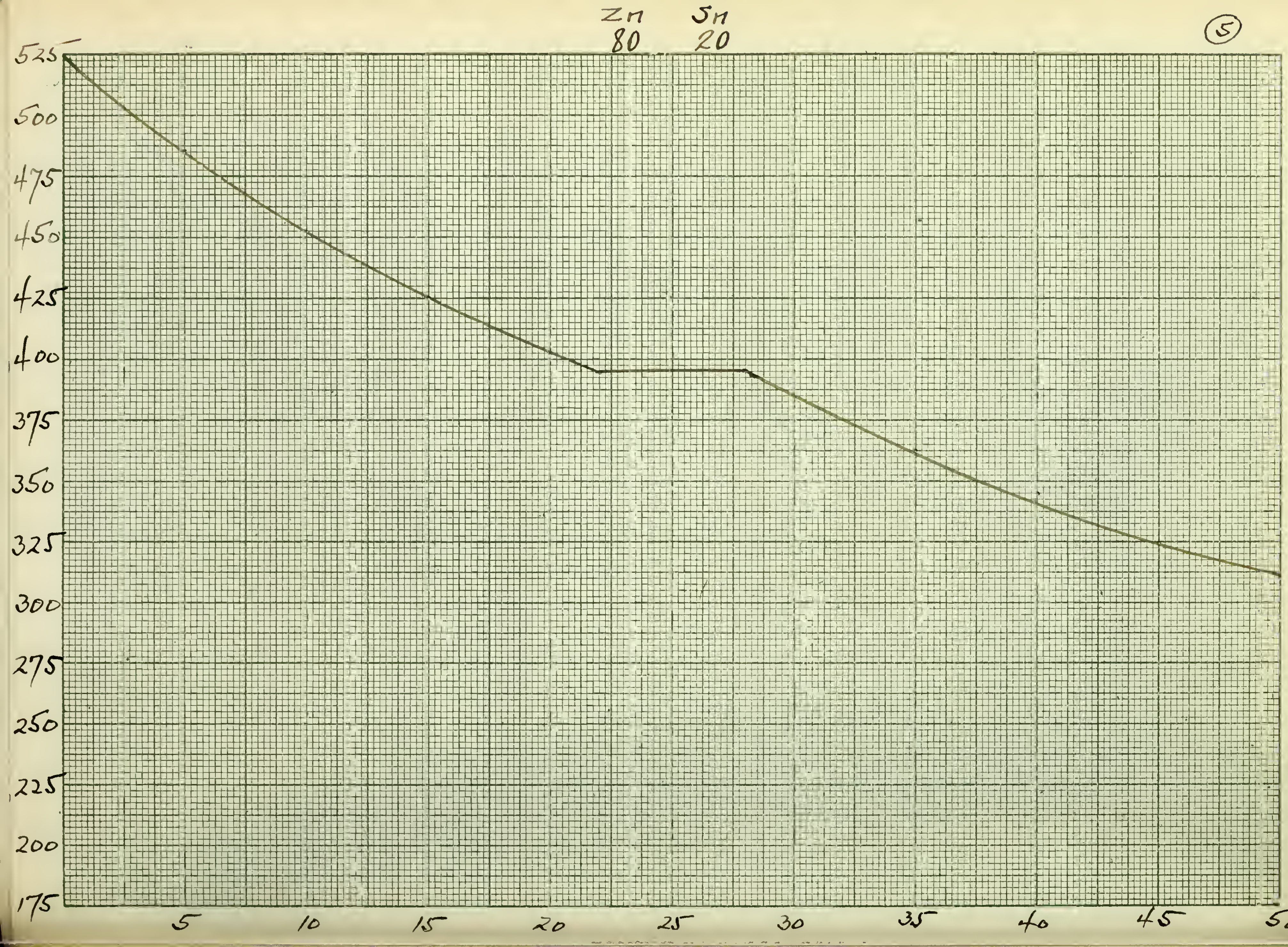

Zn
95
Sn
5
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

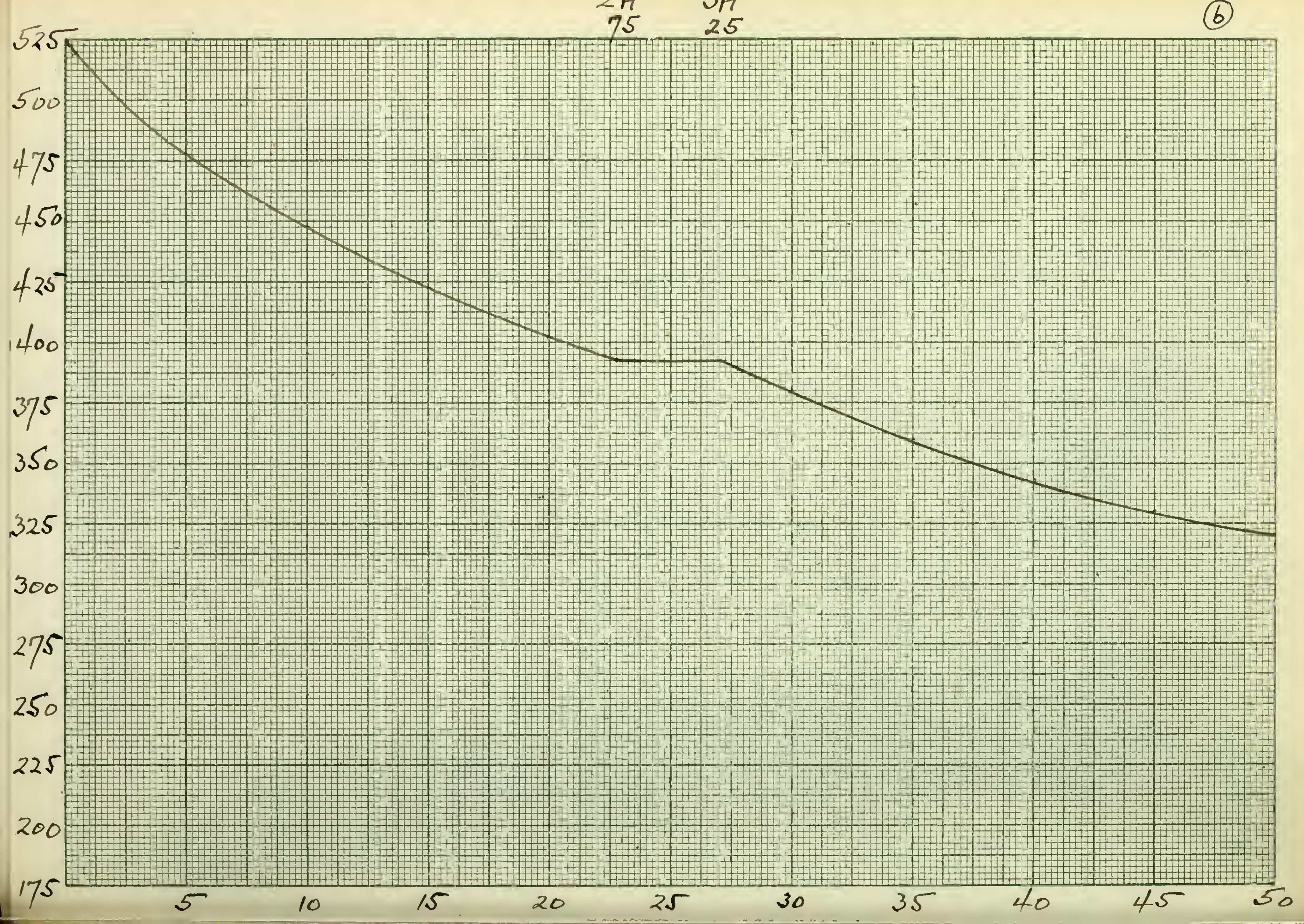


3
Zn 90
Sn 10
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

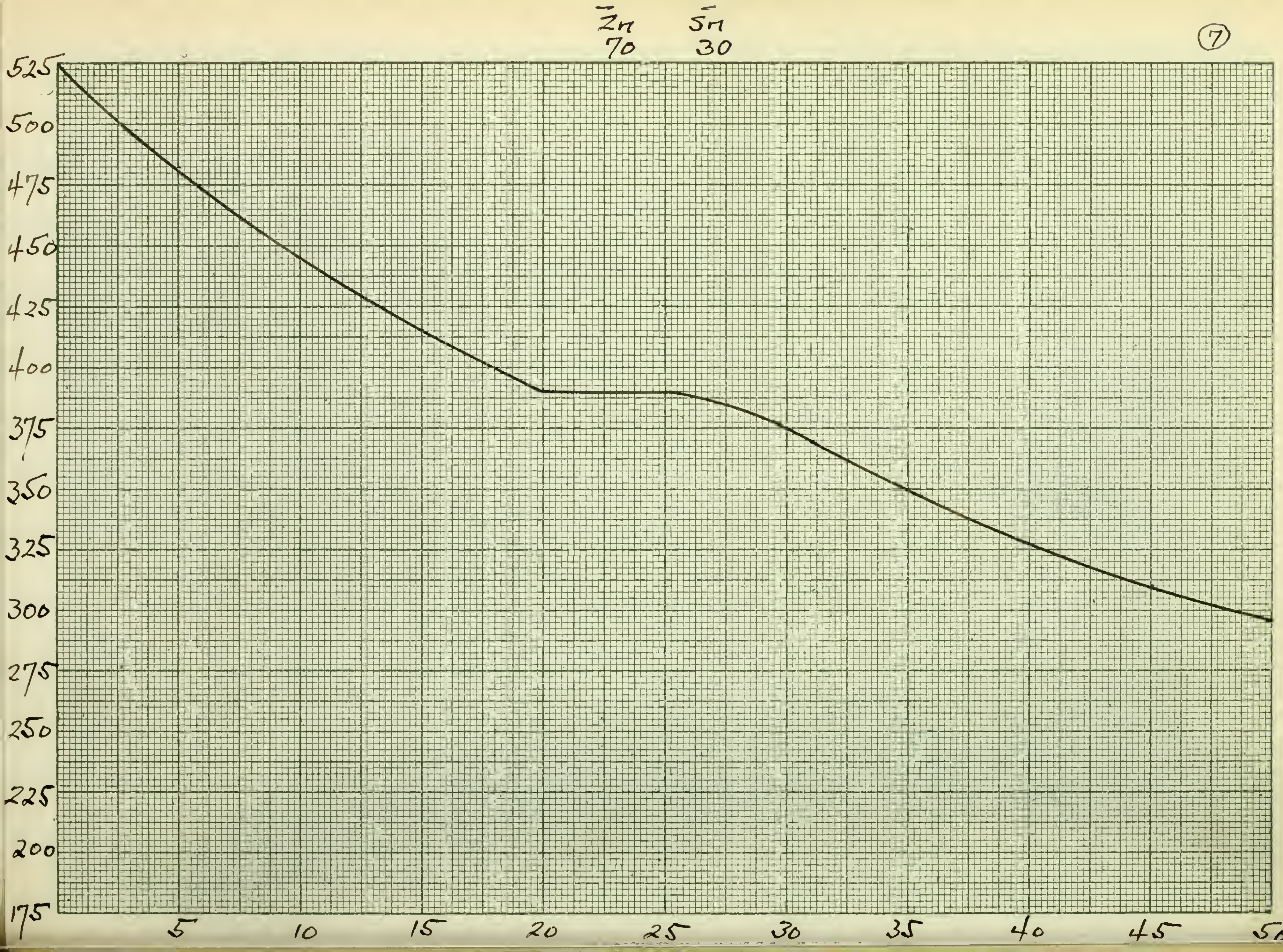

Zn
85
Sn
15
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

(5)

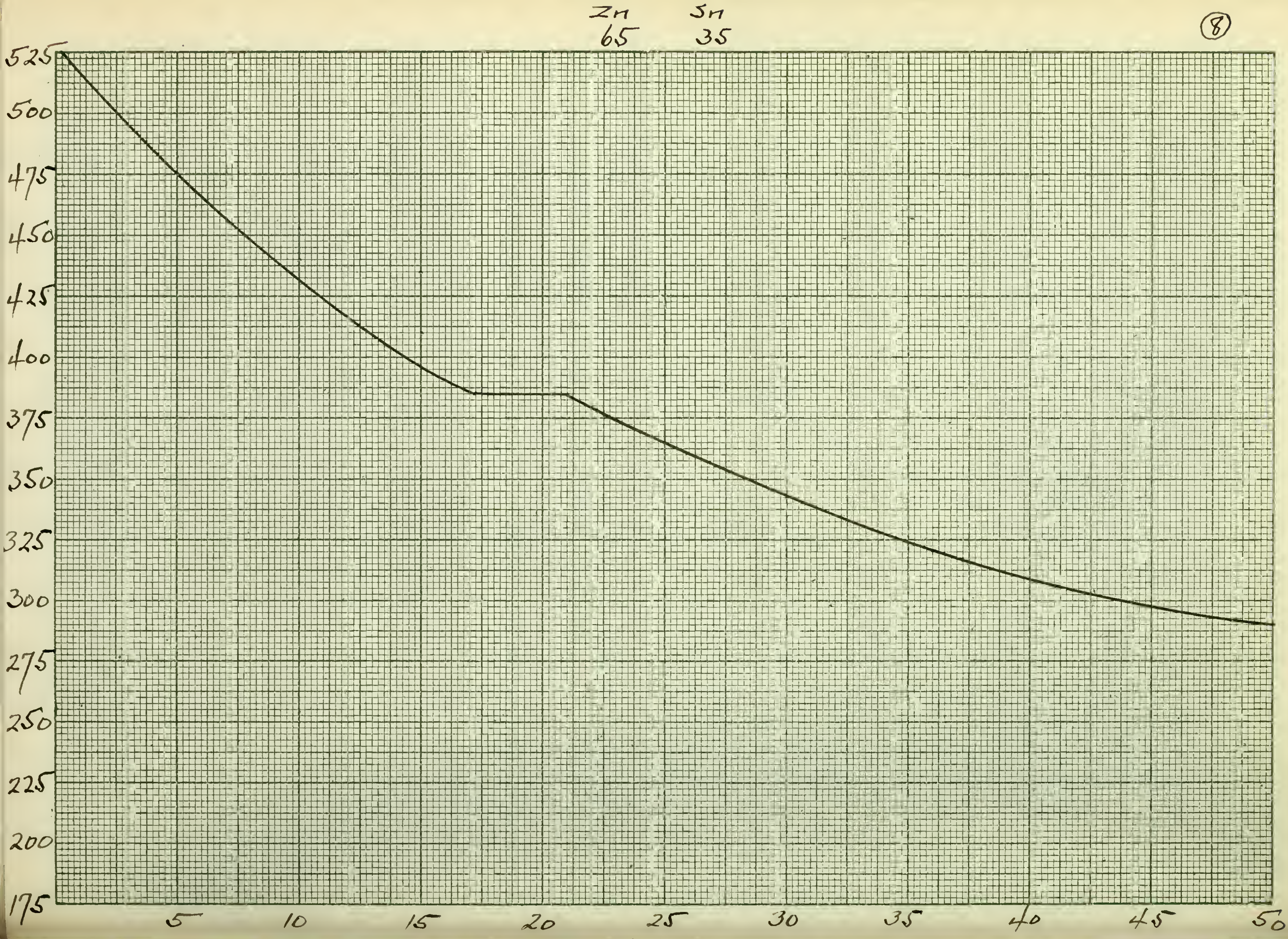

Zn 80
Sn 20
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50


6
Zn
75
Sn
25
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

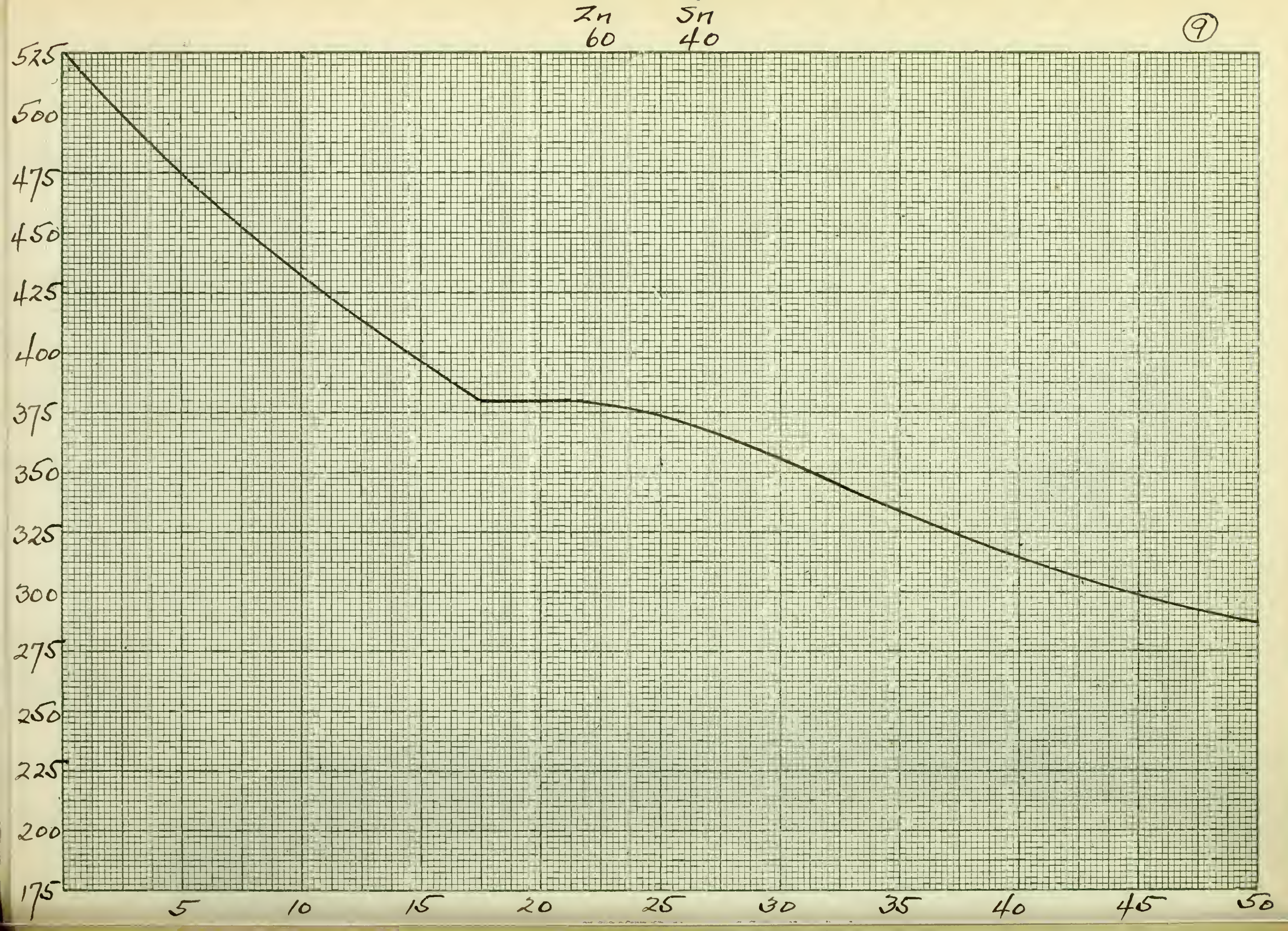
(7)



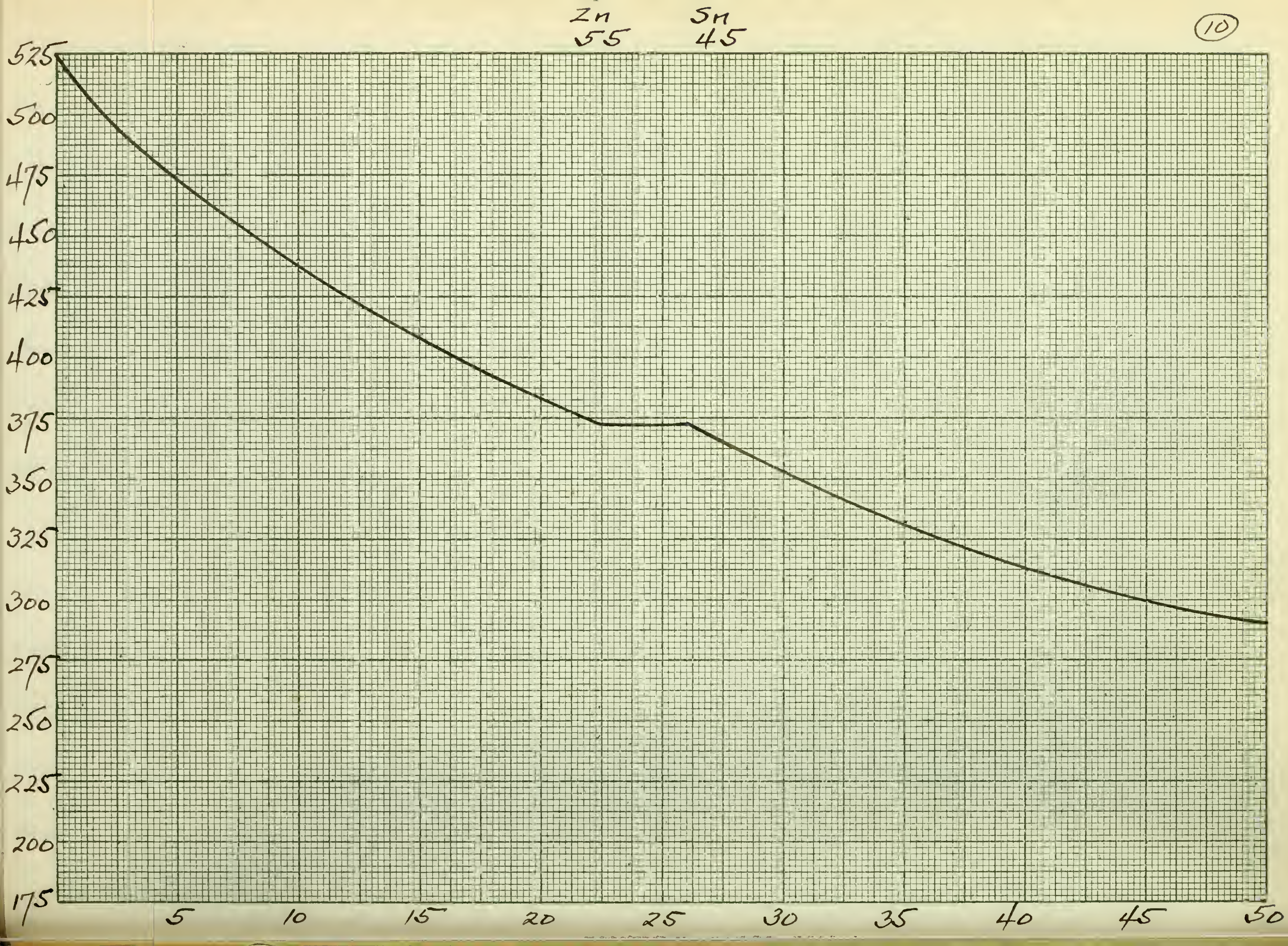
Zn 70
Sn 30
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50


Zn
65
Sn
35
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

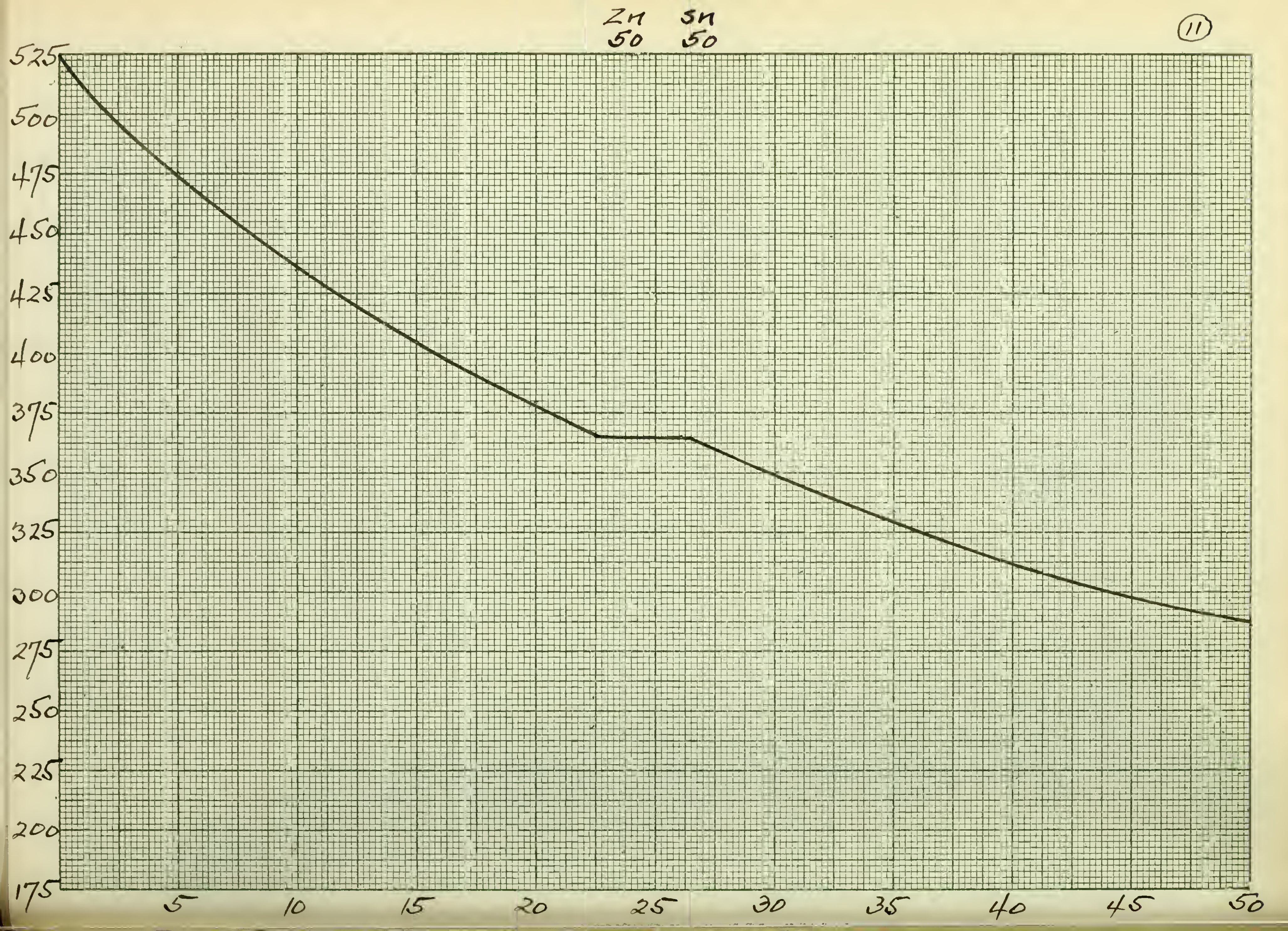
(9)



Zn
60
Sn
40
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

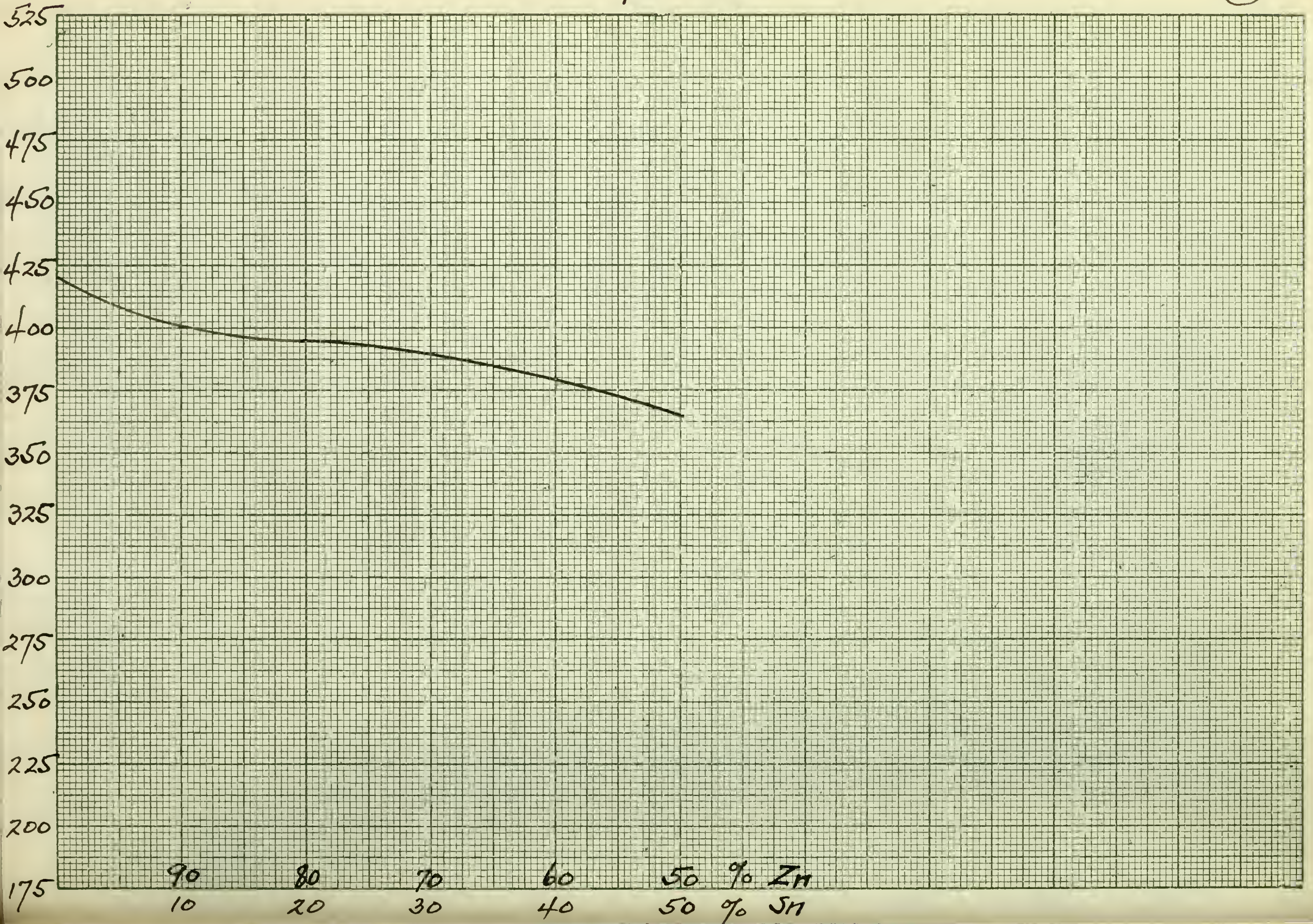

Zn
55
Sn
45
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

(11)



Zn
50
Sn
50
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

Zn - Sn Equilibrium Curve

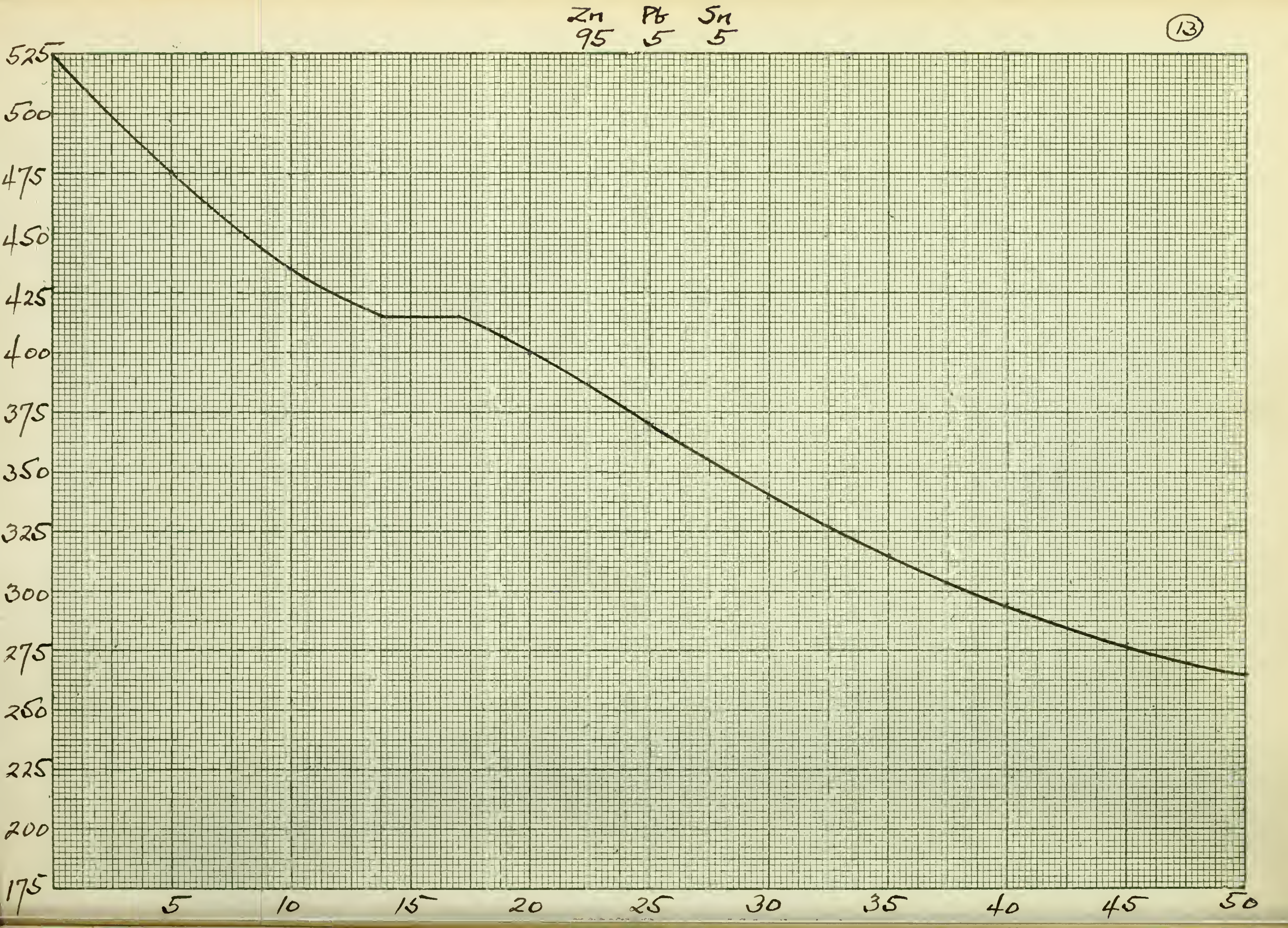


A study of the graphs for the binary system, Zn - Sn, readily shows that as the percentage of Zinc decreased and that of Tin increased the melting points decreased in value. This is to be expected when a substance of a low melting point, Sn at 327 C, is added to one of a higher melting point, Zn at 419 C and, since a flattening of the curve took place but once in each instance, it follows that Zn and Sn are soluble in each other in all proportions considered.

The following summary will briefly indicate the melting points of the different alloys:-

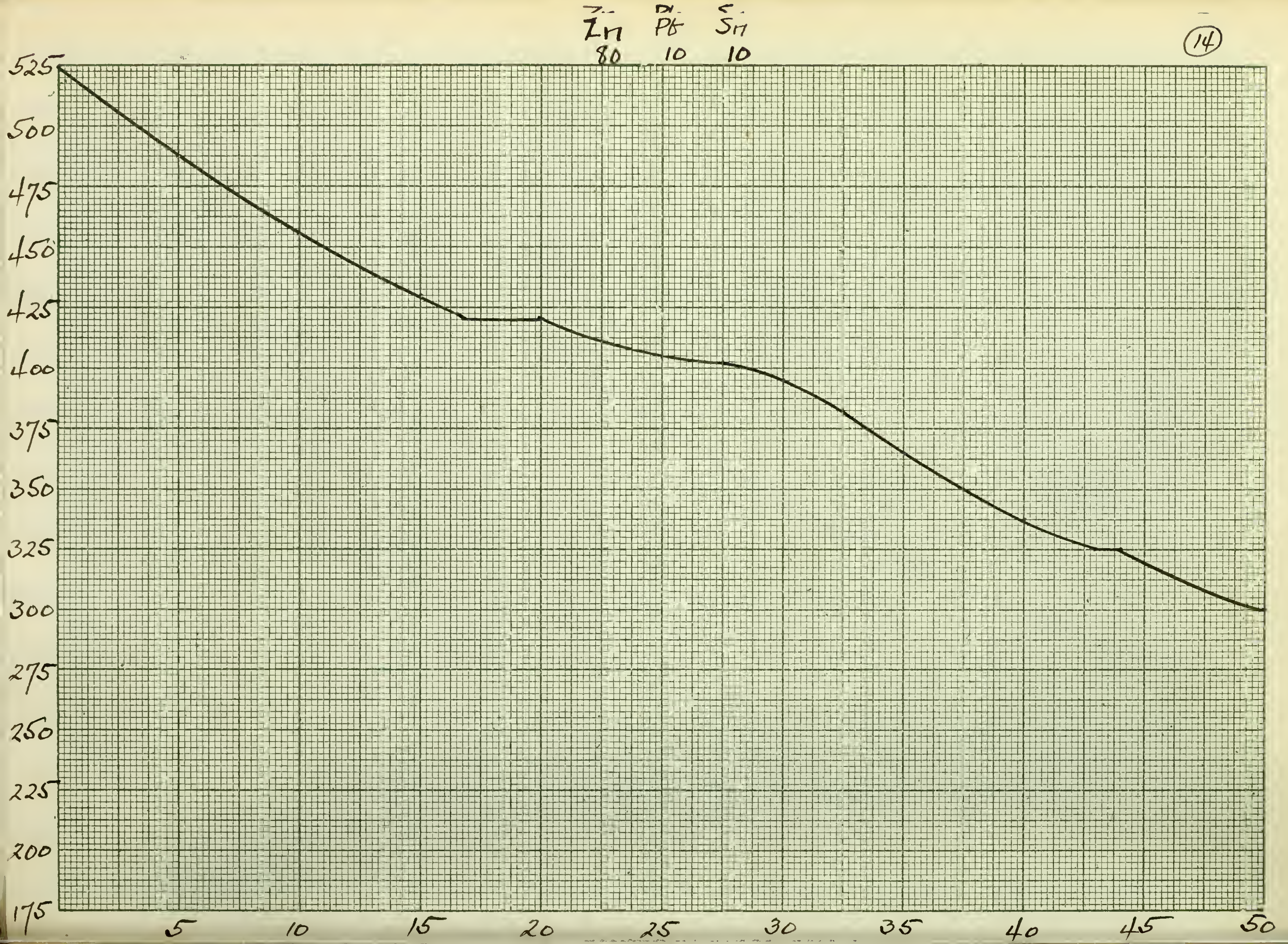
Zinc %	Tin %	MP C
100	--	419
95	5	410
90	10	400
85	15	397
80	20	395
75	25	393
70	30	390
65	35	385
60	40	380
55	45	373
50	50	365

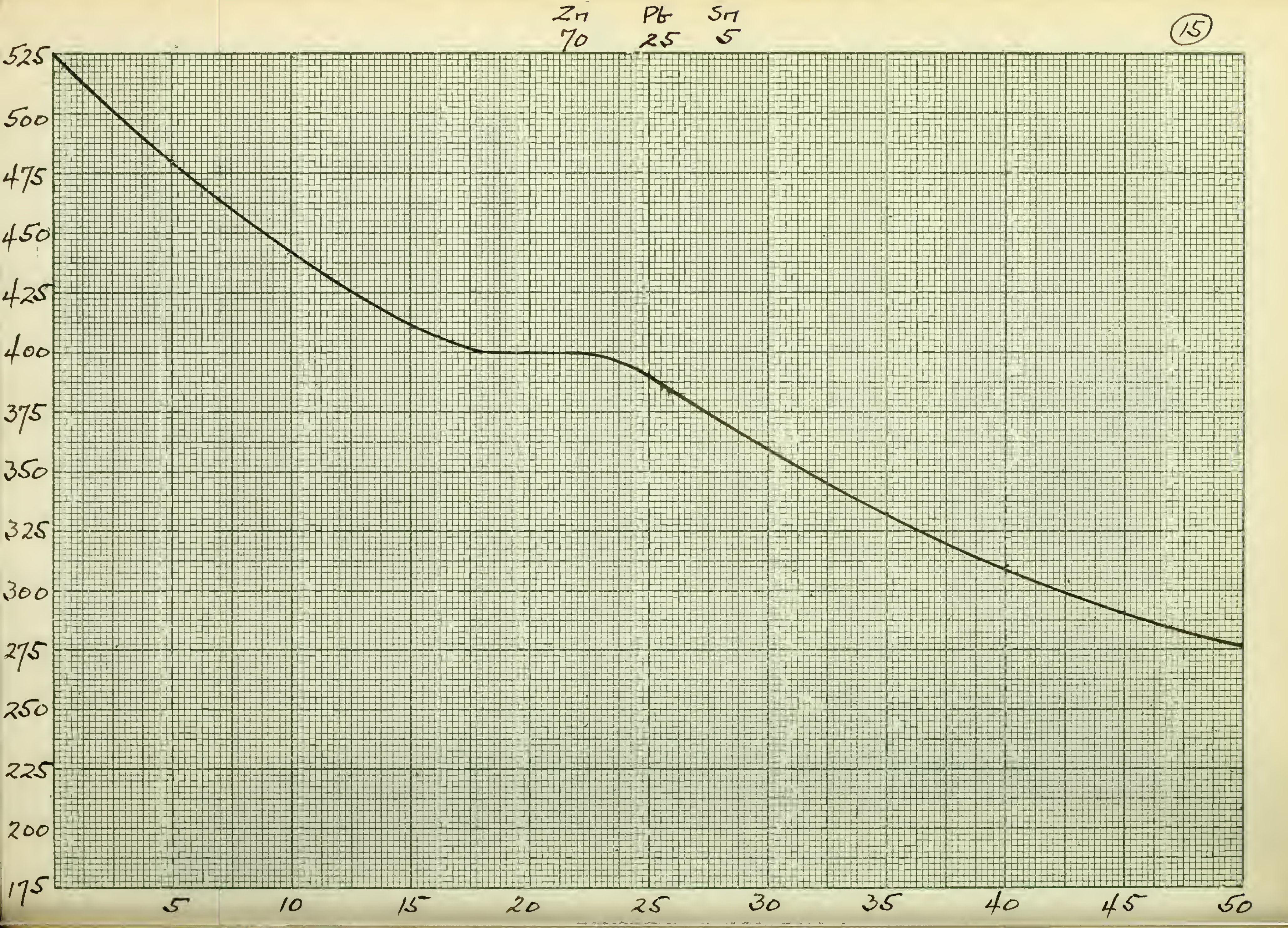
These results have also been plotted -- temperature against percentage composition, on the Zn - Sn equilibrium curve, which will give a visualized representation of the same data (See graph No, 12.)

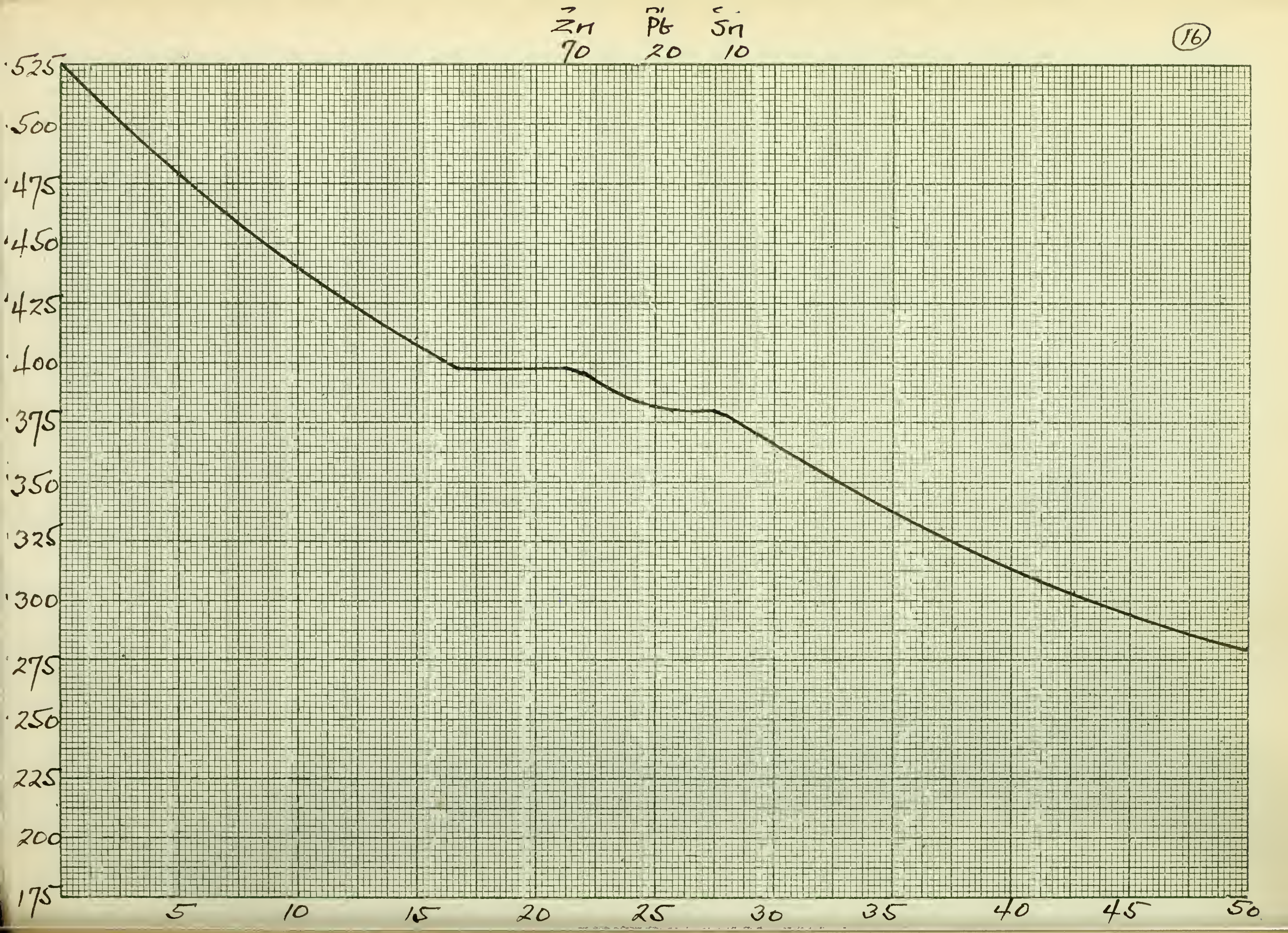


Zn 95
Pb 5
Sn 5
13
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

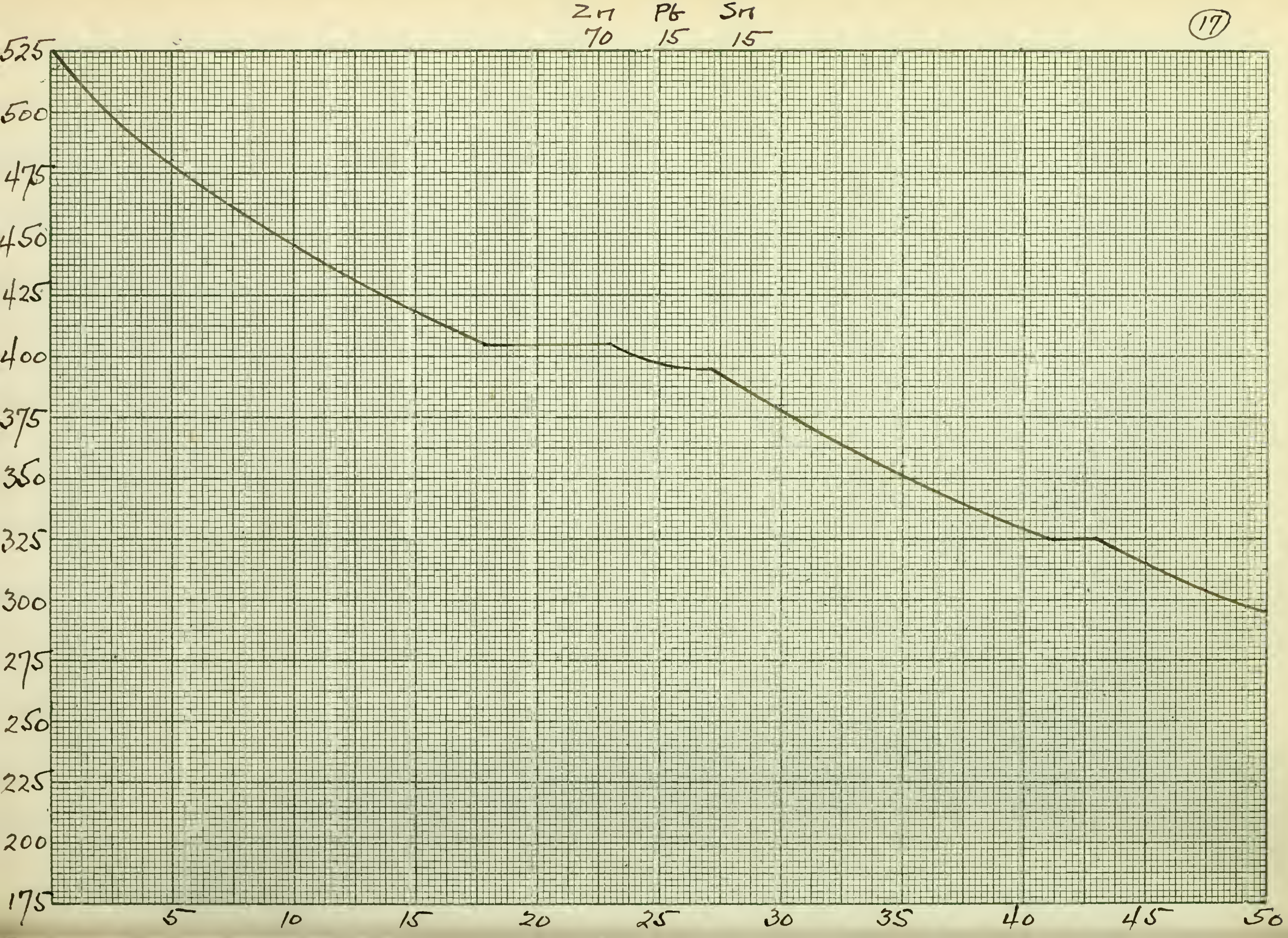
(14)


Zn Pb Sn
80 10 10
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

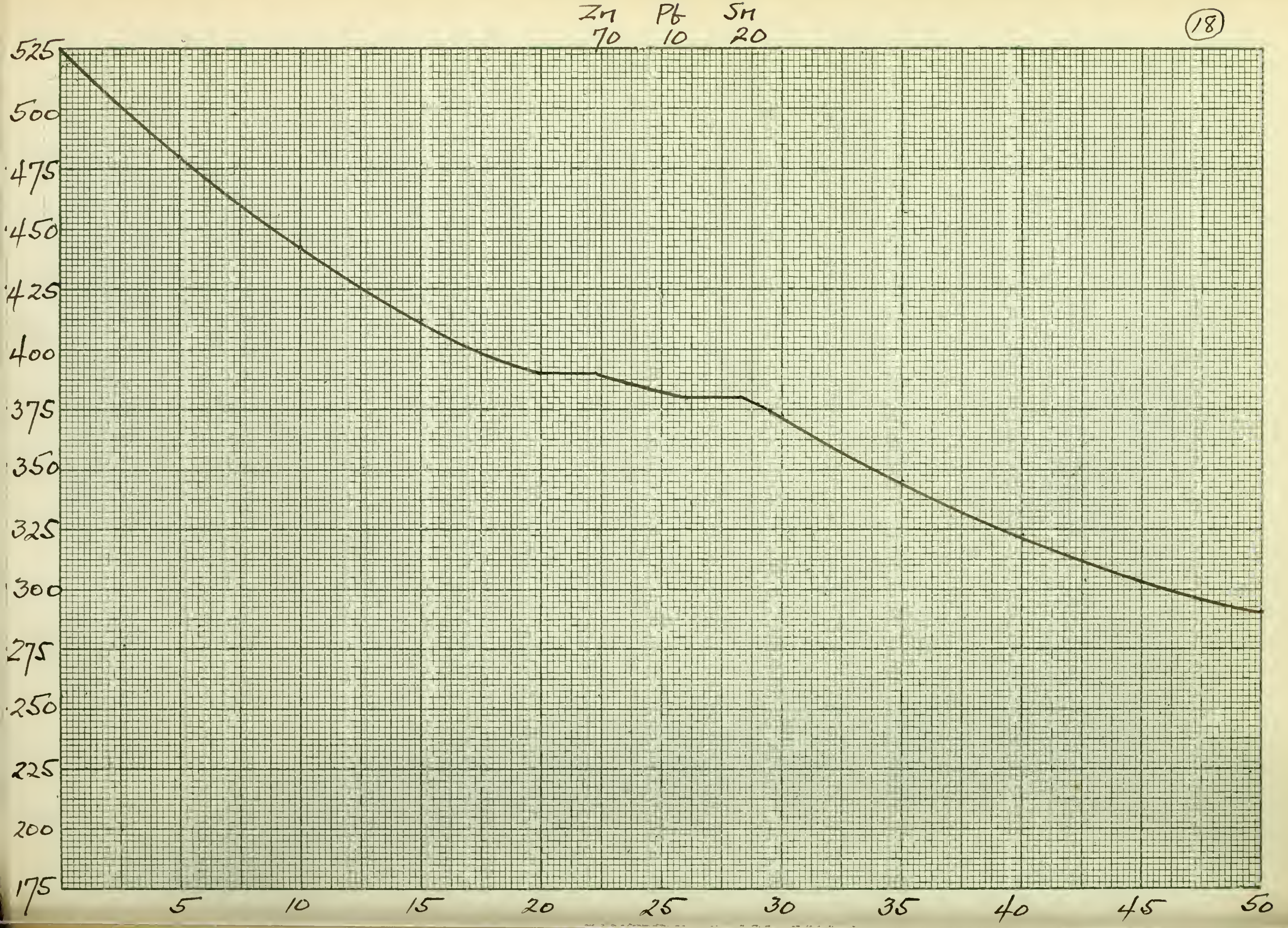

Zn 70
Pb 25
Sn 5
15
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50



16
Zn 70
Pb 20
Sn 10
.525
.500
.475
.450
.425
.400
.375
.350
.325
.300
.275
.250
.225
.200
.175
5
10
15
20
25
30
35
40
45
50

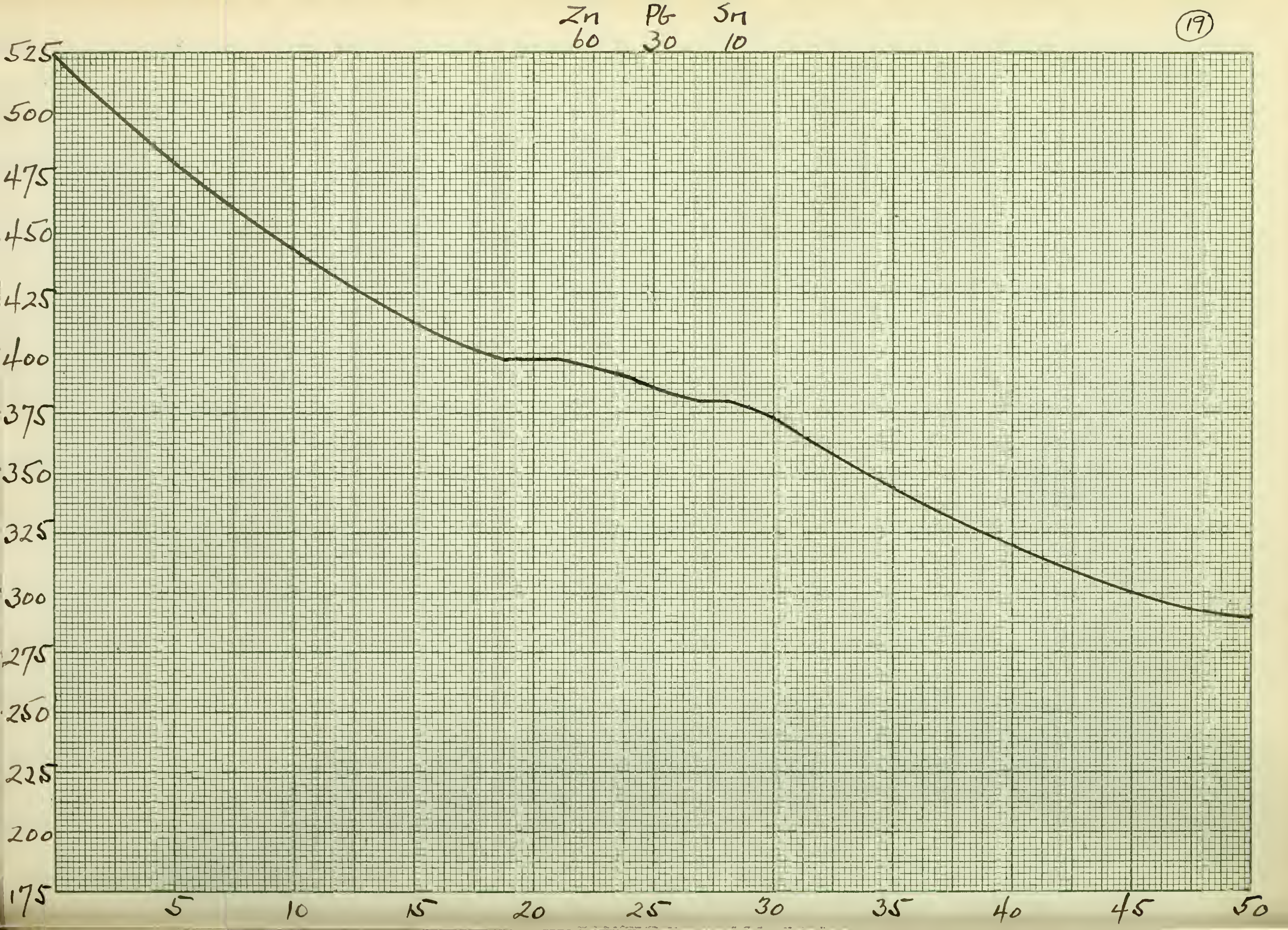

Zn 70
Pb 15
Sn 15
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

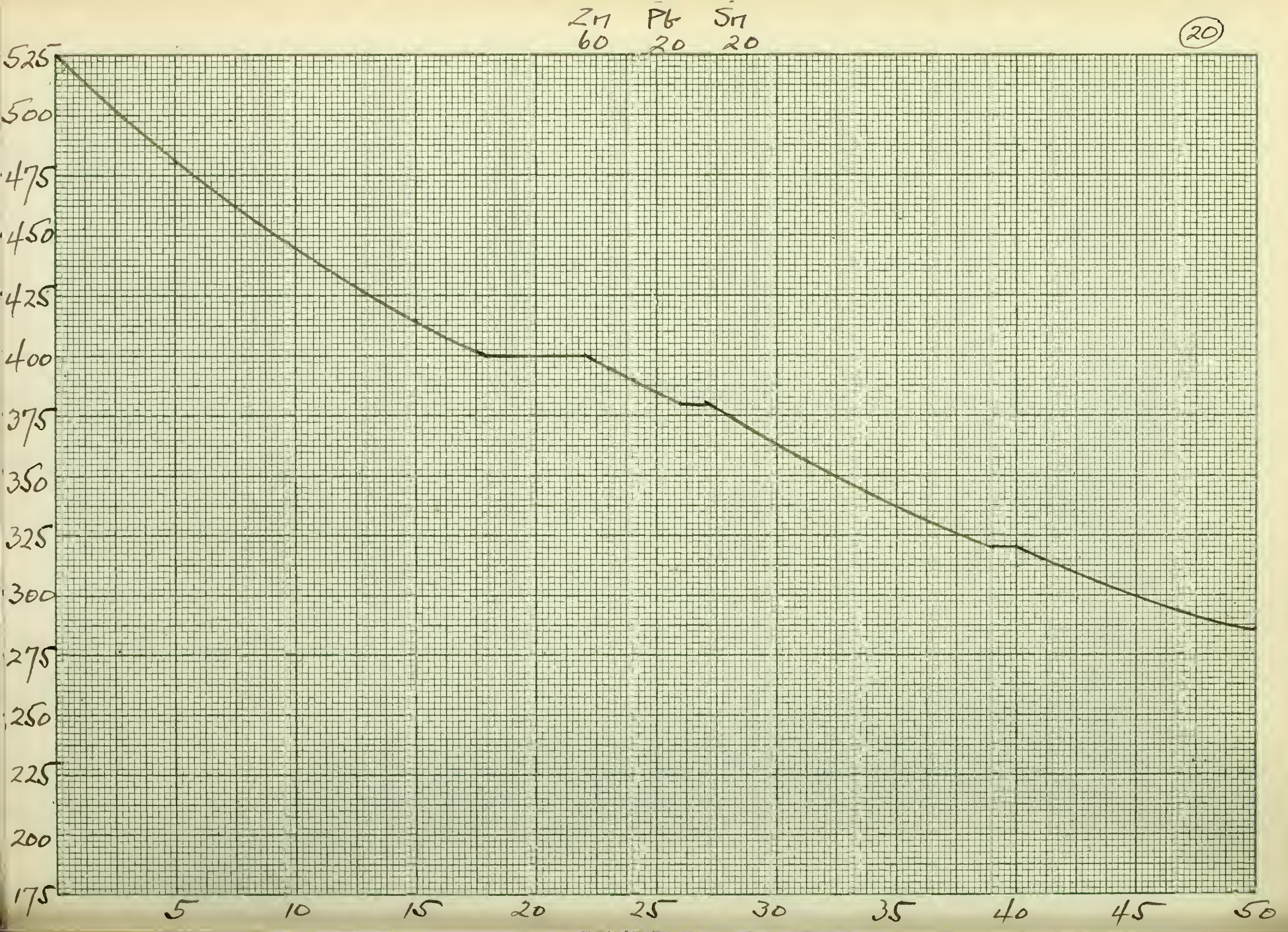
(18)



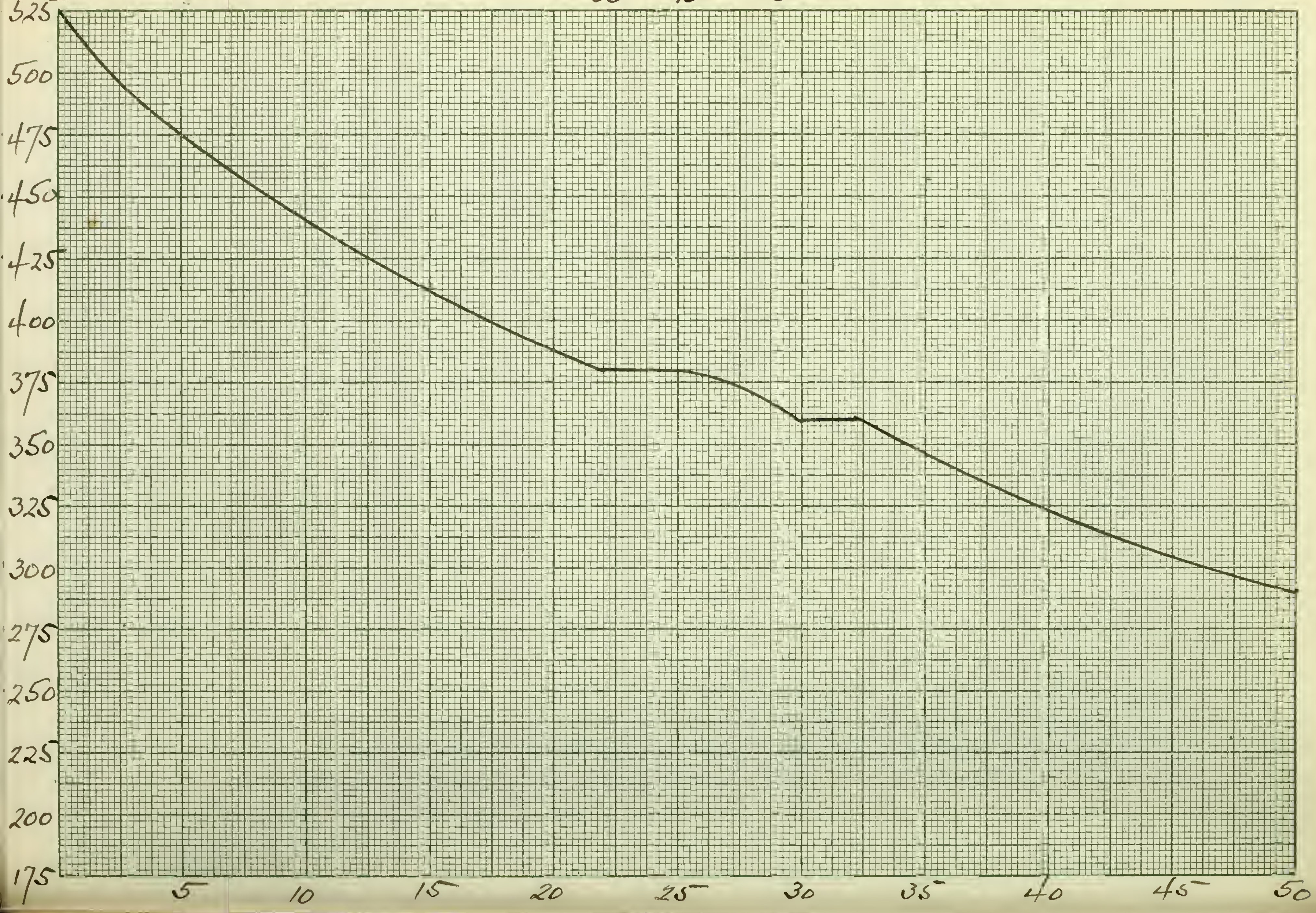
Zn 70
Pb 10
Sn 20
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

(19)

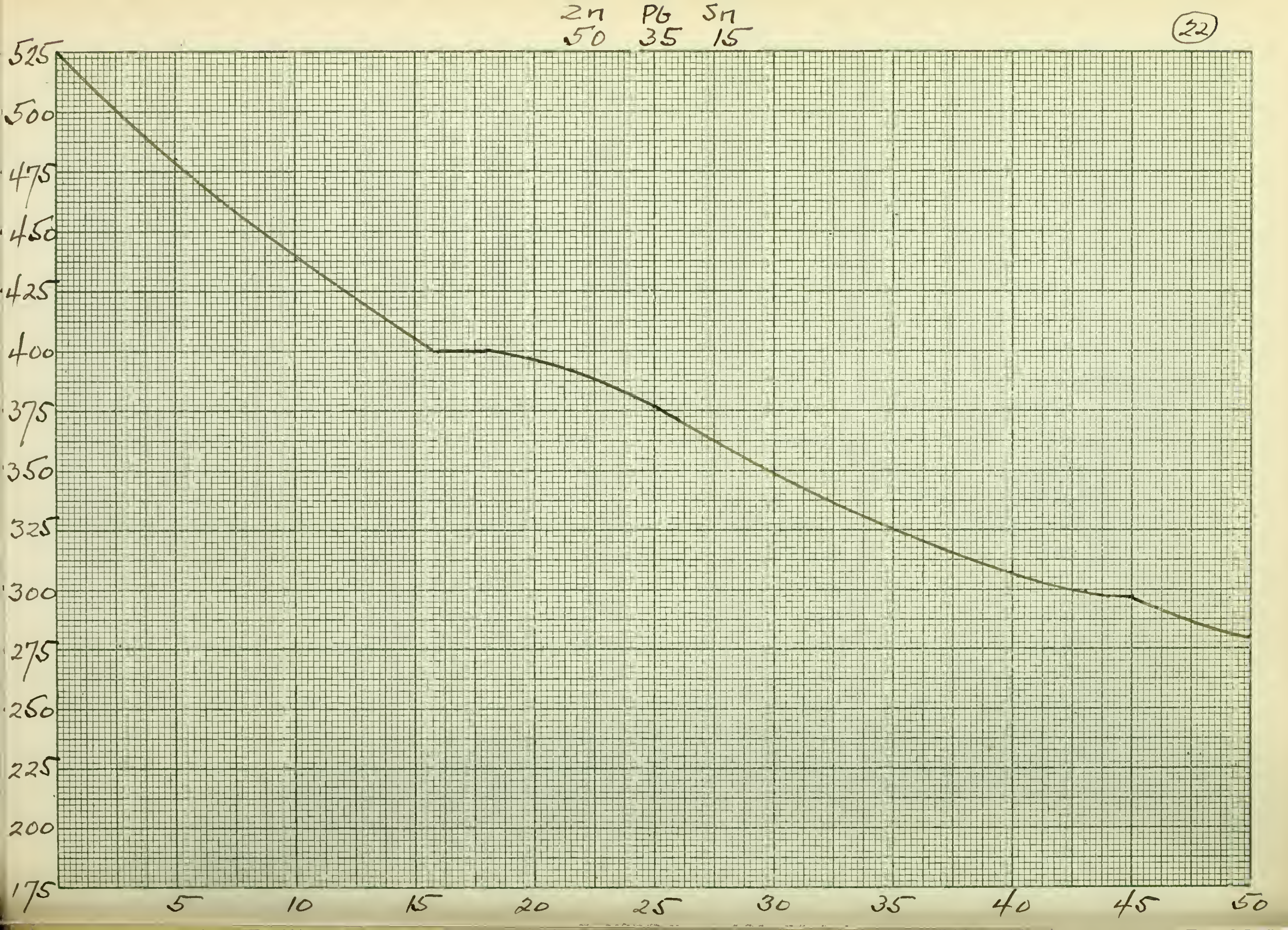

Zn 60
Pb 30
Sn 10
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

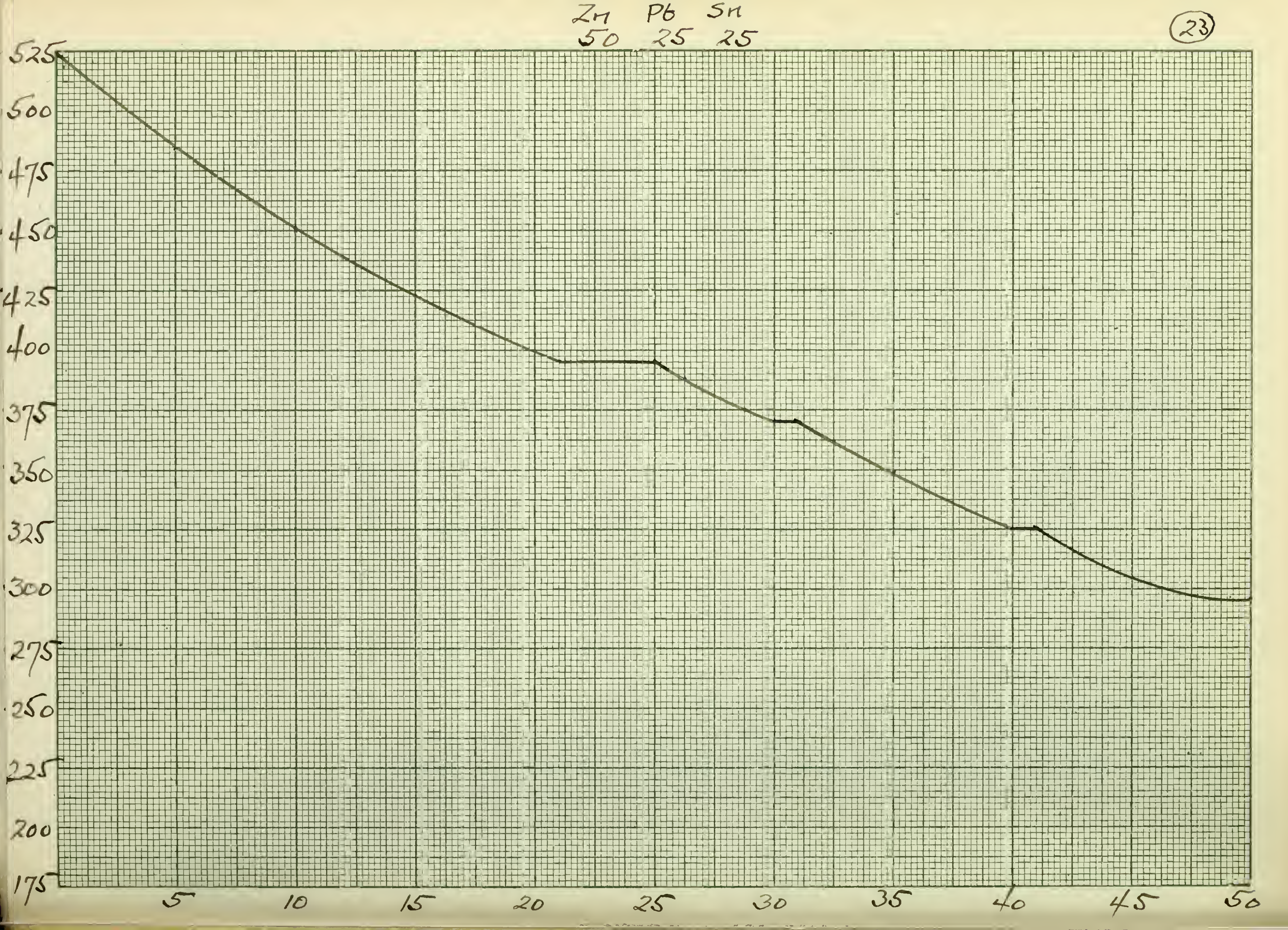

Zn 60
Pb 20
Sn 20
(20)
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

Zn 60 Pb 10 Sn 30



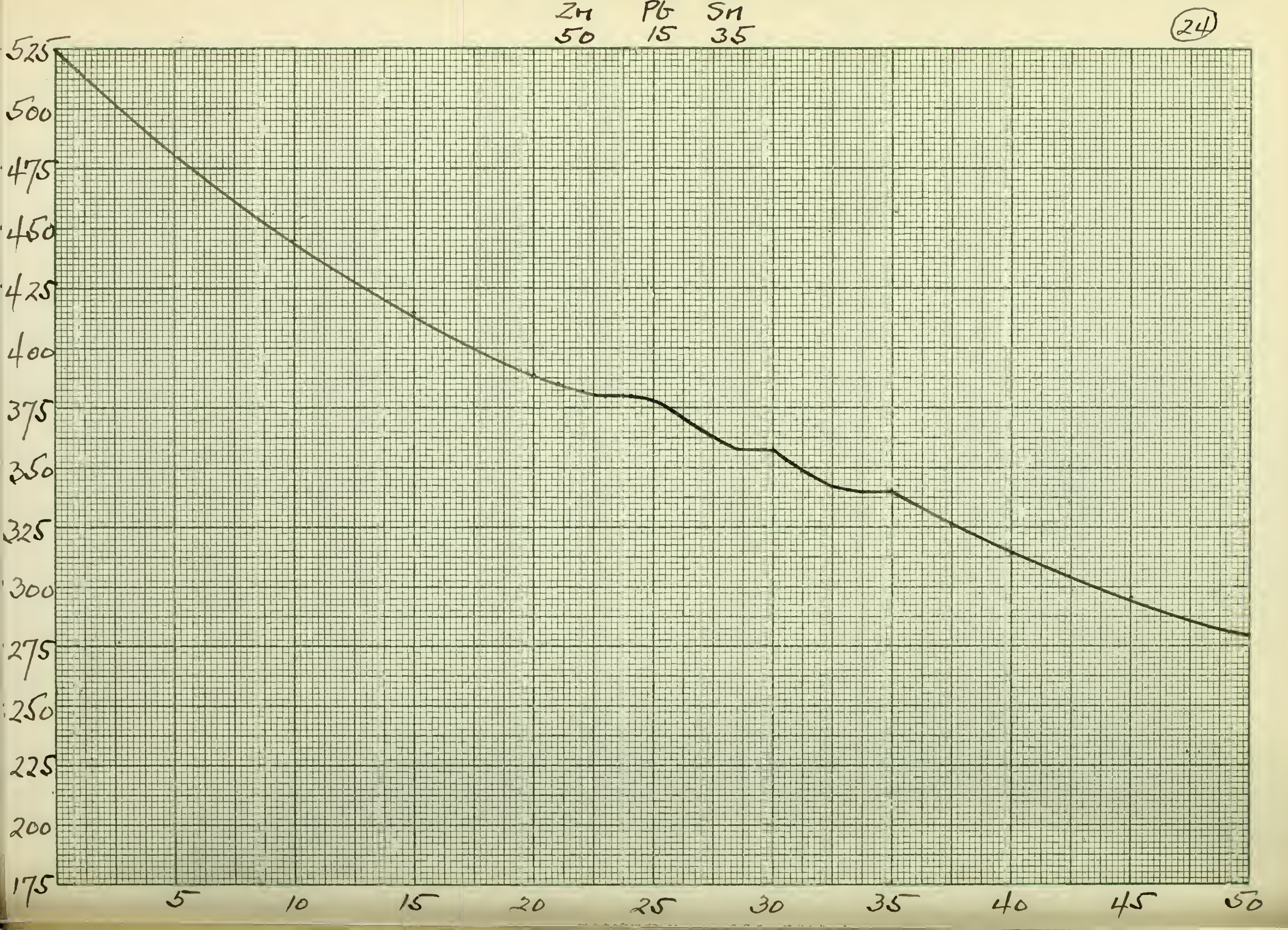
(22)


Zn Pb Sn
50 35 15
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50



Zn Pb Sn
50 25 25
(23)
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

(24)



Zn 50
Pb 15
Sn 35
525
500
475
450
425
400
375
350
325
300
275
250
225
200
175
5
10
15
20
25
30
35
40
45
50

The binary system is comparatively simple. When the ternary system however is considered, a number of irregularities are at once evident. Zn - Pb - Sn are not soluble in each other in all proportions. This is borne out by the fact that in some instances the curve has flattened out in as many as three distinct places.

A composition of 90% Zn - 5% Pb - 5% Sn was uniformily soluble. The next graph (number 14) shows a remarkable change. Some of this solution seems to have solidified at 419 C, the melting point of Zinc, a second solidification at 405 C, and a third at 325 C, close to the melting point of Lead. From these facts, as verified in other alloys, are shown that some of the Zinc went out of solution in its pure state and solidified at 419 C; that a solution of some mixture, presumably Zn, Pb, and Sn, solidified at 405 C; and finally that some of the uncombined Lead went out of solution very close to its usual melting point, 327 C. From such data we must gather that a mixture of that composition upon complete solidification is anything but uniform in texture. Strangely enough graph 15 shows that the constituents are completely soluble in one another. The very next composition, graph 16, shows another radical change. In the latter instance another three fold solidification took place - no separation of a pure element this time, but rather three distinct combinations solidifying at 397 C, 380 C, and 295 C respectively. A natural inference would be that all the Zinc had fallen out in the first two separations and that in the latter case lead and tin alone had combined.

A comparison of #16 and #17 shows that although the lead control of the latter was more than that of the former, yet the

initial melting point of the former was higher than that of the latter; while the final solidification of the latter is higher than that of the former. The most logical explanation of this phenomena seems to be that in #17 a larger part of the lead, in an uncombined state, fell out at 325 C - near its ordinary melting point.

Number 18 in which 70% Zn was also employed, shows that no lead fell out. This is not unusual since the lead content of the alloy was only 10%. There was a double solidification, at 390 C and at 380 C. This held true over a very small range of temperature only 10 . In #17 there was a marked tendency toward a close double solidification, which probably took place in a small degree, the heat radiation of the furnace being too rapid for the thermocouple to make the proper registration.

60% Zinc was contained in the alloys indicated on graphs # 19, #20, and #21. It is of interest to note the similarity of graphs #16 and #19, the former containing 70% Zinc and the latter 60% Zinc. In both cases the first two solidifications took place at the same temperatures 395 C and 380 C and practically during the same time intervals. Why this should be true is difficult to determine. The latter alloy had 10% lead and that may be one of the contributing factors. Of the three alloys containing 60% Zinc only one of them, #20, shows any evidence of a third solidification, at 320 C which was very likely caused by a freezing out of some lead and tin.

Alloys #22, #23, and #24 contained 50% Zinc. #22, with 35% lead, shows a deposition of that metal alloyed with tin at 300 C. The initial freezing point was at 400 C which is higher than for the other two alloys. #23 and #24, on the other hand, show a

triplicate solidification in each instance. This is undoubtedly due to the increase of the tin content with which the Zinc and some lead readily alloyed themselves. In #23 some lead fell out in an isolated way. That this did not hold true for #24 is evident from the fact that the freezing temperature there was 340 C which is 13 higher than the melting point of pure lead. This shows that some zinc must have had an influence in the rise of temperature.

The following summary will briefly indicate the melting points of the different alloys:-

%	%	%	Solidifications.		
Zn	Pb	Sn	1	2	3
90	5	5	415	---	---
80	10	10	420	405	325
70	25	5	400	---	---
70	20	10	397	380	295
70	15	15	405	395	325
70	10	20	390	380	---
60	30	10	397	380	---
60	20	20	400	380	320
60	10	30	380	360	---
50	35	15	400	---	297
50	25	25	395	370	325
50	15	35	380	360	340

That Zn - Pb - Sn will not combine in all proportions is amply borne out by the evidence of the above experiments. This, likewise, indicates that there must be a wide range in the texture

of the alloys -- some will have higher tensile strengths, some will withstand more compression, than others. Their molecular structures must greatly vary as a microscopic study would undoubtedly reveal. This much given as a clue as to what might be expected, further investigations are necessary to determine certain other qualities more definitely.